

# CONTENTS

|              |   |
|--------------|---|
| Introduction | 1 |
|--------------|---|

## 1

### THE FIRST LAW OF THERMODYNAMICS

|                                               |   |
|-----------------------------------------------|---|
| 1.1. Systems and Characteristic Parameters    | 3 |
| 1.2. The Work Principle for Adiabatic Systems | 5 |
| 1.3. The Zeroth Law of Thermodynamics         | 6 |
| 1.4. The First Law of Thermodynamics          | 7 |

## 2

### THE SECOND LAW OF THERMODYNAMICS

|                                                                                  |    |
|----------------------------------------------------------------------------------|----|
| 2.1. Quasi-equilibrium Processes                                                 | 10 |
| 2.2. Kelvin's Formulation of the Second Law and the Principle<br>of Carathéodory | 10 |
| 2.3. The Entropy                                                                 | 13 |

## 3

### THE GIBBS EQUATION

|                                                                        |    |
|------------------------------------------------------------------------|----|
| 3.1. The Differential Form of the Gibbs Equation                       | 19 |
| 3.2. The Integration of the Gibbs Equation—the Gibbs–Duhem<br>Equation | 22 |
| 3.3. Thermodynamic Potentials and Cross Relations                      | 24 |

## 4

### ENTROPY CHANGE IN IRREVERSIBLE PROCESSES

|                                                                                       |    |
|---------------------------------------------------------------------------------------|----|
| 4.1. Increase of Entropy in an Adiabatic Process                                      | 31 |
| 4.2. Conditions of Equilibrium for an Adiabatic System                                | 36 |
| 4.3. Examples of the Increase in Entropy During Adiabatic Irre-<br>versible Processes | 38 |
| 4.4. Entropy Changes in Isothermal Processes                                          | 42 |

## 5

ISOTHERMAL EQUILIBRIA AND  
CHEMICAL THERMODYNAMICS

|                                                  |    |
|--------------------------------------------------|----|
| 5.1. Conditions of Equilibrium for Free Energy   | 46 |
| 5.2. Chemical Transformations and Equilibria     | 47 |
| 5.3. Consideration of a Mechanicochemical System | 51 |
| 5.4. The Chemical Potential                      | 52 |

## 6

FLOWS AND FORCES IN THE THERMODYNAMICS  
OF IRREVERSIBLE PROCESSES

|                                                                                              |    |
|----------------------------------------------------------------------------------------------|----|
| 6.1. Formal Treatment of Flows                                                               | 60 |
| 6.2. Conservative and Nonconservative Continuous Systems                                     | 63 |
| 6.3. Flows in Stationary States                                                              | 66 |
| 6.4. Treatment of Thermodynamic Forces                                                       | 68 |
| 6.5. An Example of the Dependence of Flow on Force:<br>Simple Diffusion in a Binary Solution | 70 |

## 7

## ENTROPY PRODUCTION IN CONTINUOUS SYSTEMS

|                                                    |    |
|----------------------------------------------------|----|
| 7.1. The Gibbs Equation for Local Quantities       | 74 |
| 7.2. The Local Entropy Production                  | 78 |
| 7.3. Entropy Production in Electrochemical Systems | 81 |
| 7.4. Appendix                                      | 82 |

## 8

THE PHENOMENOLOGICAL EQUATIONS RELATING  
FLOWS AND FORCES; ONSAGER'S LAW

|                                                                                                                                  |    |
|----------------------------------------------------------------------------------------------------------------------------------|----|
| 8.1. Introductory Remarks                                                                                                        | 85 |
| 8.2. The Phenomenological Equations                                                                                              | 86 |
| 8.3. The Curie-Prigogine Principle                                                                                               | 88 |
| 8.4. Onsager's Law                                                                                                               | 89 |
| 8.5. Chemical Kinetics and Phenomenological Equations.<br>The Principle of Detailed Balance and Its Relation<br>to Onsager's Law | 91 |

## 9

## ISOTHERMAL DIFFUSION AND SEDIMENTATION

|                                           |     |
|-------------------------------------------|-----|
| 9.1. General Considerations               | 98  |
| 9.2. Binary Solutions                     | 100 |
| 9.3. Ternary Solutions                    | 102 |
| 9.4. Sedimentation in a Centrifugal Field | 104 |

## 10

MEMBRANE PERMEABILITY TO NONELECTROLYTES:  
DISCONTINUOUS SYSTEMS

|                                                                  |     |
|------------------------------------------------------------------|-----|
| 10.1. Transition to Discontinuous Systems                        | 113 |
| 10.2. Flows and Forces                                           | 117 |
| 10.3. Membrane Properties                                        | 119 |
| 10.4. Frictional Interpretation of Phenomenological Coefficients | 126 |

## 11

TRANSPORT PROCESSES IN CONTINUOUS SYSTEMS  
CONTAINING ELECTROLYTES: IONIC  
CONDUCTANCE AND DIFFUSION

|                                                        |     |
|--------------------------------------------------------|-----|
| 11.1. Chemical Thermodynamics of Electrolyte Solutions | 133 |
| 11.2. Irreversible Processes in Electrolyte Solutions  | 139 |

## 12

ELECTROCHEMICAL PROCESSES IN  
DISCONTINUOUS SYSTEMS

|                                                              |     |
|--------------------------------------------------------------|-----|
| 12.1. The Dissipation Function                               | 149 |
| 12.2. Electrokinetic Phenomena                               | 153 |
| 12.3. Liquid-Junction Potentials                             | 159 |
| 12.4. Frictional Interpretation of Permeability Coefficients | 163 |
| 12.5. Composite Membranes                                    | 173 |

## 13

## SYSTEMS WITH TEMPERATURE GRADIENTS

|                                               |     |
|-----------------------------------------------|-----|
| 13.1. Thermal Diffusion in Continuous Systems | 181 |
| 13.2. Thermal Osmosis                         | 185 |
| 13.3. Thermoelectricity                       | 190 |

## 14

RELATIONS BETWEEN CHEMICAL REACTIONS AND  
DIFFUSION PROCESSES

|       |                                                                |     |
|-------|----------------------------------------------------------------|-----|
| 14.1. | Chemical Reactions and Steady-State<br>Concentration Gradients | 200 |
| 14.2. | Diffusion with Chemical Reaction: A Carrier System             | 203 |
| 14.3. | Phenomenological Description of Active Transport               | 208 |

## 15

## STATISTICAL DERIVATION OF ONSAGER'S LAW

|       |                                                                        |     |
|-------|------------------------------------------------------------------------|-----|
| 15.1. | Theory of Fluctuations                                                 | 217 |
| 15.2. | The Principle of Microscopic Reversibility and<br>Onsager's Hypothesis | 225 |

## 16

STATIONARY STATES: THE PRINCIPLE OF  
MINIMUM ENTROPY PRODUCTION

|       |                                                             |     |
|-------|-------------------------------------------------------------|-----|
| 16.1. | Principle of Minimum Entropy Production                     | 229 |
| 16.2. | Stability of Stationary States                              | 231 |
| 16.3. | The Principle of Least Dissipation and Biological Stability | 233 |
|       | List of Symbols                                             | 236 |
|       | References                                                  | 239 |
|       | Index                                                       | 245 |